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## QUANTIFICATION OF MAJOR COMPONENTS EMITTED FROM SMOLDERING COMBUSTION OF WOOD

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**Abstract**—The major condensable products ( $-45^{\circ}\text{C}$ ) from smoldering combustion of ponderosa pine sapwood have been identified and quantified. Methylene chloride extracts of the condensate, as well as nonextracted condensate, were analyzed by gas chromatography/mass spectrometry (GC/MS). Non-condensed gases were analyzed by gas chromatography/flame ionization detector (GC/FID). About 83–93% of the carbon consumed in the fires has been accounted for. Variability in yields of compounds between individual fires ranged from 3 to 39% for most components, which indicates the fires and the analytical procedures are reproducible. The major products in the condensate (as percentage by weight of wood consumed) are acetic acid (0.44%), methanol (0.43%), vinyl acetate (0.3%), pyruvic aldehyde (0.12%) and acetol (0.2%). Vinyl acetate does not appear to have been reported as a major component of wood smoke. The other major products are known components of wood smoke. The molar ratios of emitted condensable products to carbon monoxide have been calculated and may form a future basis for assessing the exposure of humans to these products in large-scale biomass fires.

**Key word index:** Semi-volatile compounds, air toxics, smoldering combustion, biomass burning, ponderosa pine.

### INTRODUCTION

Biomass fires emit a complex mixture of trace gases and particulate matter into the atmosphere. Many of the compounds may be toxic and/or carcinogenic, especially if exposure levels are high (Ward *et al.*, 1993). Presently, there is very little knowledge concerning the concentrations of exposure to firefighters and residents from wildland fire smoke. Methods for measuring these exposures are limited. In addition, some of the emitted low molecular weight hydrocarbons and particulate matter are major air pollutants and/or greenhouse gases (Crutzen and Andreae, 1990).

The burning of biomass is widespread, with more than six million hectares burned each year in the United States (Ward *et al.*, 1993). This large area encompasses wildfires and prescribed fires. Wildfires occasionally result in poor air quality, such as in Northern California and Southern Oregon in 1987 and near Yellowstone National Park in 1988 (Ward *et al.*, 1993). However, the amount of biomass burned in the United States accounts for only 2–3% of the biomass burned globally (Hao and Liu, 1994). Most of the biomass burning occurs in the tropics, and may create serious air quality and health problems. High ambient concentrations of carbon monoxide (CO) have been measured in urban areas of the Amazon

Basin in Brazil, mostly caused by biomass burning in the Amazon forests (Ward *et al.*, 1992). The use of fires has significantly increased in tropical countries during the last two decades because of rapid changes of land use practices (Hao and Liu, 1994). Fires are widely used for deforestation, shifting cultivation, domestic energy consumption and clearing of agricultural residues.

Considerable work has been done to identify and quantify the condensable volatile fraction of smoke. Methoxylated phenols and related compounds have been measured in particulates and gaseous phases in the plumes emitted from wood stoves (Hawthorne *et al.*, 1989; Simoneit *et al.*, 1993), and in urban air over cities where wood burning occurs (Hawthorne *et al.*, 1992). Some of these compounds, e.g. phenol, 2-methoxyphenol and their derivatives, along with other oxygenated organics, also have been identified in smoke from smoldering combustion of wood in bench-scale fires (Edye and Richards, 1991). The major components of the condensates were attributed to pyrolysis of lignin and polysaccharides of wood. Smoldering combustion is also the major process for emitting lower molecular weight compounds during biomass fires (Lobert *et al.*, 1991).

We report in this paper the yields of major components from pyrolysis of ponderosa pine sapwood. Several significant condensable, but relatively volatile

compounds not previously measured in wood smoke have been quantified, such as vinyl acetate and acetol. Vinyl acetate has not been detected before in wood smoke. An improved procedure is developed to analyze polar compounds, such as carboxylic acids. The reproducibility of the emission yields from bench-scale fires is investigated. Preliminary ratios are calculated between the concentrations of emitted oxygenated organics and those of CO, because CO is often measured in samples collected from biomass fires in the field whereas the condensable products are rarely measured. In this way, it may be feasible to estimate the concentrations of condensable products from the concentrations of CO in ambient air and the levels of human exposure to these compounds.

## EXPERIMENTAL METHODS

### Experimental system

The bench-scale experiments of smoldering combustion of ponderosa pine wood are similar to the ones described by Edye and Richards (1991), with improvement in the control of air flow and the addition of a Tedlar bag to collect a portion of the gases emerging from the cold traps. Ponderosa pine (*Pinus ponderosa*) sapwood was ground to pass a 1 mm sieve in a Wiley mill. Approximately 20 g of a sample was placed in a ceramic dish (10.5 cm diameter, 1 cm depth), and heated under a 10 A electrical radiant heating coil (5 cm above the wood surface) inside an inverted glass funnel (32 cm diameter). The funnel was set on a bench (which was covered by a sheet of aluminium foil) with a 5 cm  $\times$  0.5 cm gap to allow for air intake. The neck of the funnel was connected via a downward sloping corrugated Teflon tube (0.95 cm i.d.) to two glass traps in series immersed in an ethylene glycol-water bath at  $-45^{\circ}\text{C}$ . Smoke was drawn through the traps by an SKC Airchek sampler at a flow rate of  $0.2 \text{ l min}^{-1}$ . An aliquot of smoke after emergence from the cold trap was collected in a Tedlar bag by an SKC Personal Air Sampler at  $45 \text{ ml min}^{-1}$  for analysis of gases  $\text{CO}_2$ , CO,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$ . Three experiments were conducted.

The fuel was allowed to smolder for 35 min, during which time any occasional flaming was extinguished by temporarily reducing the current to the radiant heating coil. The final products of combustion were a mixture of ash, char and some unburned fuel ( $< 6 \text{ g}$ ), a creosote oil or tar on the inside of the funnel ( $< 2 \text{ g}$ ), condensed volatile compounds in the two cold traps ( $\sim 7 \text{ g}$ ) and in the Teflon corrugated tube, and non-condensable gases in the Tedlar bag. The contents of the two cold traps and the Teflon corrugated tube (a light brown translucent liquid) were combined and stored at  $-20^{\circ}\text{C}$  for later analysis. Noncondensable components were collected in Tedlar bags. There was a very small yield of particulate matter and no attempt was made to separate the particulates either from the condensates or the noncondensates.

### Extraction of condensates

Aliquots (1.0 ml) of each smoke condensate sample were extracted into methylene chloride in an extraction vial. A solution (0.1 ml) of d5-phenol in methylene chloride ( $0.143 \text{ mg ml}^{-1}$ ) was added as an internal standard to the extraction vial, followed by additional methylene chloride (1.0 ml). The vial was capped and shaken by hand for 5 min, assuring complete emulsification of the two phases. The vial was then centrifuged and the methylene chloride phase was removed by syringe and transferred to an amber vial. The

aqueous phase was then further extracted with two 1 ml portions of methylene chloride. More than 90% of the compounds were removed by three successive extractions of methylene chloride. The methylene chloride phases were combined in the amber vial and stored at  $-20^{\circ}\text{C}$ .

### GC/MS analysis of condensable compounds

The first standard solution was prepared by dissolving weighted amounts of the compounds not marked with an asterisk in Table 2, together with d5-phenol, in water. This solution was diluted to five different concentrations, and each was extracted three times with methylene chloride as described above. The extracts were analyzed by gas chromatography/mass spectrometry (GC/MS) (procedure (a) below) to establish linearity. A response factor (the integrated area of the ion current of the molecular ion of the analyte and the concentration of the internal standard against the concentration of the analyte and the area of the ion current of the molecular ion of the internal standard) for each analyte was calculated. A mean response factor for each compound was determined from the five standard solutions. The methylene chloride extracts from the condensates were then analyzed by GC/MS. The products were identified with authentic compounds where possible and otherwise with literature MS data. Once the products were identified, they were quantified based on the integrated ion currents of their molecular ions relative to that of the internal standard (d5-phenol), using the above response factors. A second standard solution was prepared by dissolving weighed amounts of the compounds marked with an asterisk in Table 2, together with ethylene glycol, in water as the internal standard. This solution and four diluted standard solutions were then analyzed by GC/MS (procedure (b) below) to determine the response factors as described above. The condensates (with appropriate dilutions) were then analyzed by GC/MS in the same way.

Electron impact GC/MS analyses were performed at 70 eV with a Hewlett Packward (HP) 5890 GC interfaced to a 5970 series mass selective detector equipped with a HP 59970C MS Chemstation. Integration of molecular ions was done manually with the data system. The GC conditions, using a 1  $\mu\text{l}$  splitless injection, were as follows. (a) An HP Ultra I (25 m  $\times$  0.22 mm i.d.  $\times$  0.33  $\mu\text{m}$  film) column was used with a temperature program of  $35^{\circ}\text{C}$  for 3.4 min, a  $6^{\circ}\text{C min}^{-1}$  ramp to  $175^{\circ}\text{C}$ , followed by a  $30^{\circ}\text{C min}^{-1}$  ramp to  $300^{\circ}\text{C}$  for the methylene chloride extracts. The chromatogram is shown in Fig. 1. (b) An HP FFAP column (25 m  $\times$  0.2 mm i.d.  $\times$  0.3  $\mu\text{m}$  film cross-linked) was used with a temperature program of  $100^{\circ}\text{C}$  for 4 min, a  $6^{\circ}\text{C min}^{-1}$  ramp to  $170^{\circ}\text{C}$ , followed by a  $10^{\circ}\text{C min}^{-1}$  ramp to  $240^{\circ}\text{C}$  for the non-extracted aqueous standards and condensates. The chromatogram is shown in Fig. 2.

### GC/FID analysis of noncondensable gases

The analyses were performed on an HP 5890 Series GC with a flame ionization detector (FID). Carbon monoxide and  $\text{CO}_2$  were determined by flushing a gas sample through a 1 ml loop and injecting it onto a packed Carbosphere column (2 m  $\times$  3 mm i.d.) with a temperature program of  $30^{\circ}\text{C}$  for 6 min, followed by a  $10^{\circ}\text{C min}^{-1}$  ramp to  $90^{\circ}\text{C}$ , and held at  $90^{\circ}\text{C}$  for 16 min. The separated gases were reduced to methane by a nickel catalyst for detection by the FID. Methane, ethane and ethene were determined by flushing a gas sample through a 0.25 ml sample loop and injecting it onto a HP-1 precolumn (4 m  $\times$  0.53 mm i.d.), followed by a J&W Scientific GS-Q megabore column (30 m  $\times$  0.53 mm i.d.) with the same temperature program as described for CO and  $\text{CO}_2$ . The resulting chromatograms were integrated by the HP Chemstation software. Gas concentrations of the sample were determined by comparison with peak areas of external calibration standards. The peaks were identified by comparison of retention times with standard gases.

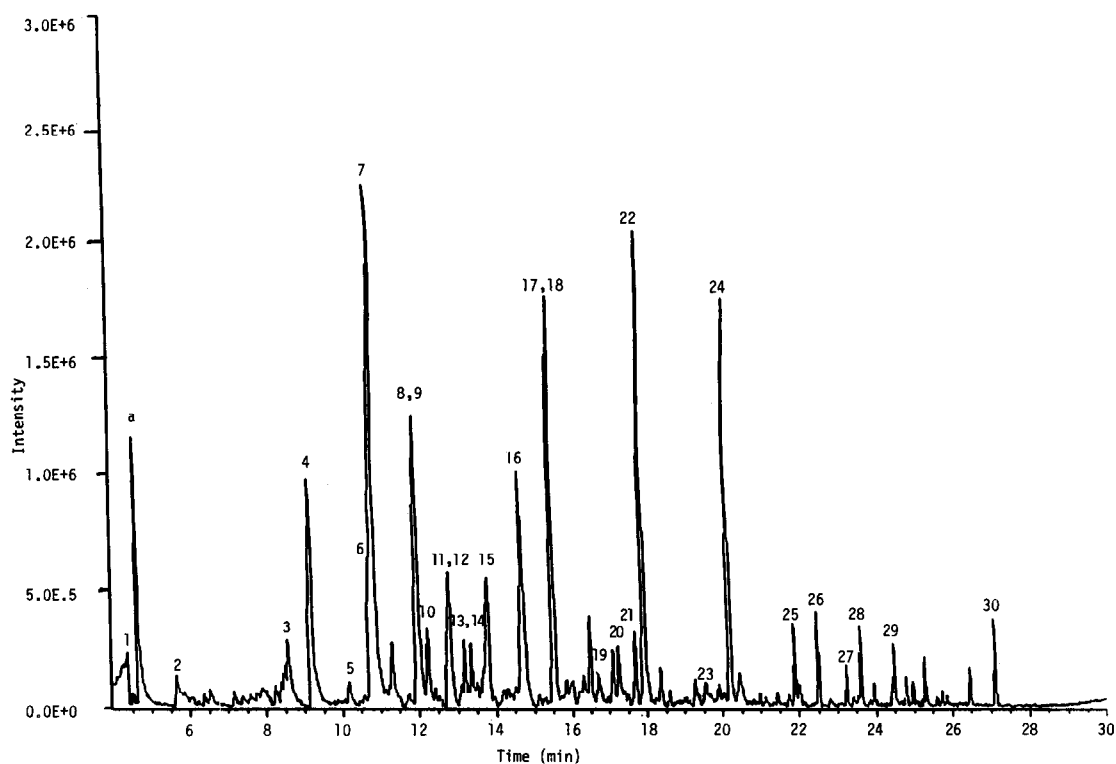


Fig. 1. Gas chromatogram of methylene chloride extract from smoke condensate, from the ultra I column. The peak numbers correspond to the numbers in Table 2. a = Solvent impurity.

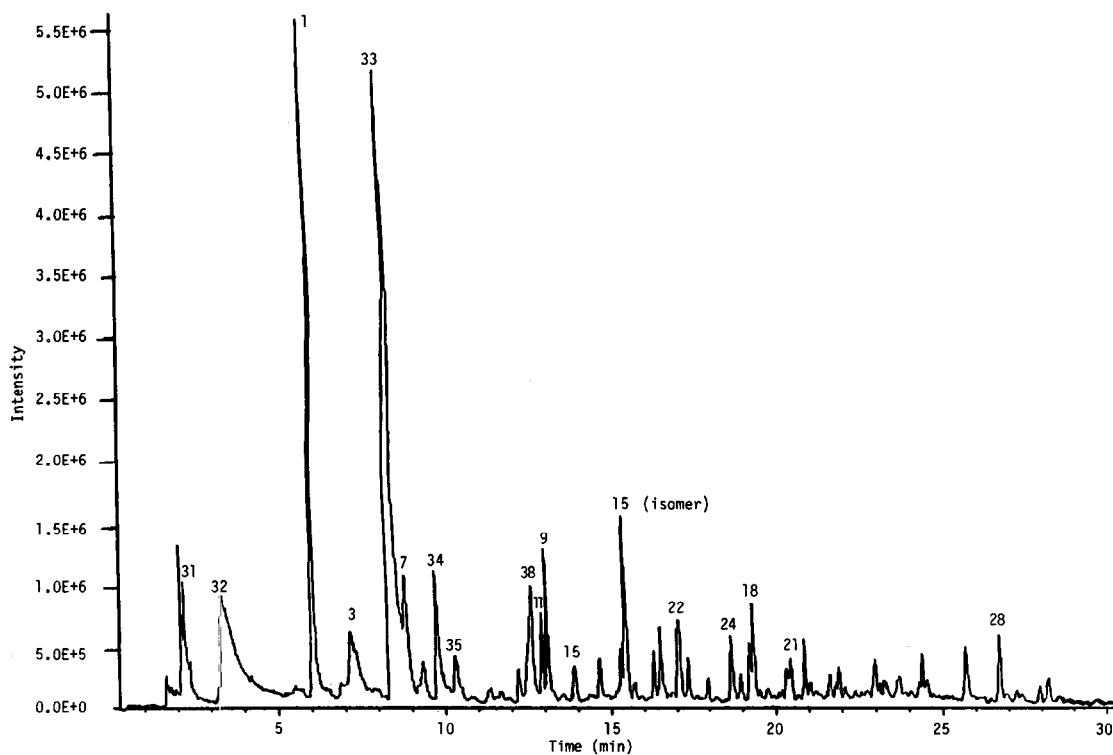


Fig. 2. Gas chromatogram of aqueous smoke condensate from FFAP column. The peak numbers correspond to the numbers in Table 2.

## RESULTS AND DISCUSSION

*Bench-scale fires*

In order to investigate the reproducibility and the extent of carbon recovery of the bench-scale fires, it was necessary to quantify two additional components of the emissions in addition to the condensable and noncondensable components. These are, respectively, the char and the products which were initially volatilized from the combustion zone, but which condensed before reaching the cold trap. We refer to the latter products as "tars". The tars were collected at two sites: (a) the condensate on the walls of the glass funnel above the combustion zone which appeared as a brown viscous liquid; (b) the condensate formed on the aluminium foil surface below the combustion zone which appeared as an almost colorless liquid. Both sources of tar were collected by dissolving in methanol (which inevitably involved some losses). The combined solutions were evaporated to dryness at 40°C in vacuo. The carbon content of tars was measured to be 48%, indicating the presence of unsaturated compounds. Preliminary GC analysis of tars, both with and without trimethylsilylation, showed a complex mixture of compounds, among which levoglucosan (mostly pyranose) predominated. It is probable that some of the volatile components of tars were lost during evaporation of the methanol solution.

The mass balances of fuel carbon for the three experiments are summarized in Table 1. Particulate yield was very low for these fires. Only 0.16 g of particulate matter was collected from a 1 µm filter. The experiments were reproducible. About 45 ± 3% of the fuel carbon was oxidized to gaseous CO<sub>2</sub>, CO, CH<sub>4</sub>, ethane and ethene, and about 1.3 ± 0.1% was converted to the condensable compounds during smoldering combustion. More than 33% of the fuel carbon was recovered as char and unburned fuel and about 5.2% as "tars". At least 83% of the fuel carbon can be accounted for. This is a low estimate since some minor condensable compounds were not quantified, and some of the components in the tar may have been lost during the analytical procedure. In addition, C<sub>3</sub>–C<sub>7</sub> alkanes, alkenes, some aromatics such as benzene and the particulates, which were not measured, may also contribute to the balance.

*Partitioning of condensates and GC/MS analysis*

The GC/MS conditions were similar to those reported earlier (Edye and Richards, 1991), but with a lower initial temperature, held before starting the temperature ramp, for analysis of compounds 1–6 (Figs 1 and 2 and Table 3) which were not detected in our previous study. The use of a more polar column with the aqueous condensates (Fig. 2) made an analysis of polar compounds more reliable (indicated by an asterisk in Table 2). This column made it possible to identify and quantify early eluting components, such as methanol and acetic acid, without solvent interference. Methanol was determined by selective ion monitoring (*m/z* 29–32) because the normal GC/MS scans commenced at *m/z* 35.

The relative response factors of most of the condensable compounds are shown in Table 2 and the relative standard deviations (RSD) for analysis of each compound in five different concentrations are mostly less than 11%. The low precision for benzoic acid analysis is associated with the poor peak shape which is generally remedied by esterification (Kakemoto, 1992), while the cause of the high variability in the vanillin analysis is not known.

*Condensable components*

The yields of major components in the smoke condensates with respect to the weight of fuel consumed are shown in Table 3. All of the products not quantified were present in minor proportion (Figs 1 and 2). The yields in Table 3 are the mean values from three separate fires. The yields of five condensable products (excluding water) exceed 1 g kg<sup>-1</sup> (i.e. 0.1% by weight). The major products are acetic acid (0.44%) and methanol (0.43%), both of which have been shown to be major early products of pyrolysis of wood (Degroot *et al.*, 1988). Acetic acid is derived from acetate ester groups in the hemicelluloses, while methanol, at least in the early stages of pyrolysis, is produced both from methyl uronic acid units in hemicelluloses and from methoxybenzene units in lignin (Degroot *et al.*, 1988). Vinyl acetate (0.30%) does not appear to have been detected as a major component of wood smoke. Vinyl acetate could be postulated as being formed by pyrolytic fragmentation of the 2-*O*- and/or 3-*O*-acetyl xylan units in the

Table 1. Mass balance of carbon

Fire	PPW 1		PPW 2		PPW 3	
	(g)	(%)	(g)	(%)	(g)	(%)
Carbon in gas phase	4.44	48.2	4.03	44.0	3.96	43.2
Carbon in condensates	0.11	1.2	0.13	1.4	0.12	1.3
Carbon in char	Not measured		3.01	32.8	3.94	43.0
Carbon in tars	0.48	5.2	0.48	5.2	0.48	5.2
Carbon in fuel	9.17		9.17		9.17	
Total carbon measured	5.03	54.8	7.65	83.4	8.5	92.7

Table 2. GC/MS reference compounds

No.	Compounds	Relative retention time†	Relative response factor‡	Relative standard deviation§ (%)
1	1-Hydroxy-2-propanone ( <i>Acetol</i> )	5.78*	0.991*	14
6	2-Cyclopenten-1-one	9.72	0.477	4.0
3	2-Furaldehyde	10.1	0.527	9.8
8	3-Oxobutanoic acid, methyl ester	11.2	0.0165	10
9	2-Furanmethanol	11.3	0.239	11
11	$\gamma$ -Butyrolactone	12.7*	1.905*	11
12	2-(5H)-Furanone	12.2	0.233	10
14	2-Acetylfuran	12.8	0.421	8.0
16	5-Methyl-2-furaldehyde	14.5	0.721	3.0
17	d5-Phenol¶	15.6	1.00	—
18	Phenol	15.6	1.30	1.7
19	<i>o</i> -Hydroxybenzaldehyde	17.1	0.633	10
20	2-Methylphenol ( <i>o</i> -cresol)	17.8	0.586	9.1
21	3 and/or 4-Methylphenol ( <i>m</i> and/or <i>p</i> -cresol)	18.3	0.723	1.5
22	2-Methoxyphenol (guaiacol)	18.6	1.17	4.6
23	Benzoic acid	20.9	0.427	26
24	2-Methoxy-4-methylphenol (4-methylguaiacol)	21.6	0.566	7.9
27	2-Methoxy-4-(1-prop-2-enyl) phenol (eugenol)	25.7	0.135	14
28	4-Hydroxy-3-methoxybenzaldehyde (vanillin)	26.3	0.470	22
31	Vinyl acetate	1.99*	0.159*	13
32	Pyruvic aldehyde	3.22*	4.08*	6
33	Acetic acid	8.01*	5.50*	16
34	Formic acid	9.51*	2.50*	5
35	Propanoic acid	10.0*	0.108*	11
36	Crotonic acid	15.1*	4.608*	11
37	Methanol	1.96*	1.32*	11
38	Ethylene glycol¶	12.4*	1.00	—

† Retention time relative to the internal standard, d5-phenol (\*ethylene glycol).

‡ Response factor relative to the internal standard d5-phenol (\*ethylene glycol).

§ Percent relative deviation for five analyses at five different concentrations, unless otherwise indicated.

¶ Internal standard.

|| Percent relative standard deviation for three analyses at different concentrations.

hemicelluloses, although there is no obvious precedent (e.g. from MS fragmentation analogy) for such a pathway. The other two major products, pyruvic aldehyde and acetol, are known pyrolysis products of polysaccharides (Faix *et al.*, 1991; Pouwels *et al.*, 1987).

Of the other products listed in Table 3, we may assume that the aromatics and probably propanoic acid are derived from lignin and most others from polysaccharides. Of the minor aliphatic products, compounds 2, 8, and 36 could be derived from either lignin or polysaccharides.

The RSD values shown in Table 3 include all the variables in the triplicate fires and in the analytical steps. Three products (compounds 9, 23, and 31) show high variability. The first two are relatively polar and the variability is probably associated with GC problems similar to benzoic acid. Vinyl acetate is a major product, but as discussed above, may not be a primary pyrolysis product and this factor may introduce an additional variability in its yield from the fires.

Many compounds analyzed, such as phenol, methoxylated phenol and their derivatives, are the same as those measured from wood stoves and in ambient air by Hawthorne *et al.* (1989, 1992). The quantitative results, however, are not comparable, because their

results are based on the mass of carbon collected on filters and the volumes of ambient air, while our results are based on the mass of the fuel consumed. The relative yields of phenols (phenol and 2, 3, and 4-methylphenol) to 2-methoxyphenol and its derivatives (2-methoxyphenol and 2-methoxy-4-methylphenol) differ in the two types of study. We found the ratio of these two classes of compounds to be 0.44:1, whereas Hawthorne *et al.* (1989) found a ratio of 0.62:1. These differences could be due to differences in sampling methods, extraction procedures, and fuels.

The recent work of Simoneit *et al.* (1993), on products of biomass combustion, closely complements our work. He reported phytosterols, lignins, diterpenoids, and phenols that range from C<sub>8</sub> to C<sub>31</sub> in the smoke from combustion of pine, and we report phenols, aldehydes, ketones, carboxylic acids, and alcohols ranging from C<sub>1</sub> to C<sub>8</sub>. The major difference between the two studies is that Simoneit *et al.* extended their measurements to include higher molecular weight products, whereas we have included the lower molecular weight range. Both studies detected 4-methylguaiacol and vanillin, although our yield for 2-methylguaiacol was seven times higher, and our yield for vanillin was double. We also detected 4-vinylguaiacol and eugenol, whereas they did not. These differences may

Table 3. Yields of components in smoke condensates

No.	Compound	Mass spectral ions†	Yield (mg kg <sup>-1</sup> )‡	Relative Standard deviation (%)
1	1-Hydroxy-2-propanone (acetol)	43, 74,* 45	2 × 10 <sup>3</sup>	33
2	2-Oxopropanoic acid, methyl ester	43, 102*	nq§	
3	3-Hydroxypropanal	43, 42, 74*	nq	
4	2-Hydroxy-3-oxobutanal	43, 102,* 42	nq	
5	3-Furaldehyde	95, 39, 96*	nq	
6	2-Cyclopenten-1-one	39, 82,* 53	1.9 × 10 <sup>2</sup>	27
7	2-Furaldehyde	39, 96,* 95	7.9 × 10 <sup>2</sup>	15
8	3-Oxobutanoic acid, methyl ester	43, 59, 116*	7.0 × 10 <sup>2</sup>	26
9	2-Furanmethanol	41, 98,* 53	2.8 × 10 <sup>2</sup>	43
10	2-Cyclopenten-1,4-dione	42, 96,* 68	nq	
11	γ-Butyrolactone	42, 56, 86*	1.7 × 10 <sup>2</sup>	10
12	2-(5H)-Furanone	55, 84,* 39	2.2 × 10 <sup>2</sup>	15
13	2-Methyl-2-cyclopenten-1-one	67, 96,* 39	nq	
14	2-Acetylfuran	95, 110,* 39	5.4 × 10 <sup>1</sup>	16
15	Angelicalactone (not alpha)	55, 98,* 42	nq	
16	5-Methyl-2-furaldehyde	53, 110,* 109	1.5 × 10 <sup>2</sup>	17
18	Phenol	94,* 66, 39	1.1 × 10 <sup>2</sup>	3
19	o-Hydroxybenzaldehyde	122,* 121, 65	1.5 × 10 <sup>1</sup>	9
20	2-Methylphenol (o-cresol)	108,* 107, 77	4.2 × 10 <sup>1</sup>	24
21	3 and/or 4-Methylphenol (m/p-cresol)	107, 108,* 77	4.4 × 10 <sup>1</sup>	23
22	2-Methoxyphenol (guaiacol)	81, 109, 124*	1.8 × 10 <sup>2</sup>	18
23	Benzoic acid	105, 77, 122*	2 × 10 <sup>1</sup>	53
24	2-Methoxy-4-methylphenol (4-methylguaiacol)	123, 138,* 95	2.6 × 10 <sup>2</sup>	25
25	2-Methoxy-4-ethylphenol (4-ethylguaiacol)	137, 152,* 77	nq	
26	2-Methoxy-4-ethenylphenol (4-vinylguaiacol)	135, 77, 150*	nq	
27	2-Methoxy-4-(1-prop-2-enyl)phenol (eugenol)	164,* 103, 77	6.8 × 10 <sup>1</sup>	14
28	4-Hydroxy-3-methoxybenzaldehyde (vanillin)	152,* 151, 81	7.6 × 10 <sup>1</sup>	17
29	2-Methoxy-4-(1-prop-1-enyl)phenol	164,* 103, 77	nq	
30	2-Methoxy-4-(prop-1-en-3-one)phenol¶	178,* 135, 107	nq	
31	Vinyl acetate	43, 86,* 42	3 × 10 <sup>3</sup>	51
32	Pyruvic aldehyde	43, 72,* 42	2 × 10 <sup>3</sup>	13
33	Acetic acid	43, 45, 60*	4.4 × 10 <sup>3</sup>	29
34	Formic acid	46, 45, 44	9.7 × 10 <sup>2</sup>	24
35	Propanoic acid	45, 74,* 73	2.5 × 10 <sup>2</sup>	22
36	Crotonic acid	39, 86,* 41	6.8 × 10 <sup>1</sup>	10
37	Methanol	31, 29, 32*	4.3 × 10 <sup>3</sup>	37

† The most abundant peaks in decreasing order. The molecular ion is indicated by \*.

‡ The mean yield of three separate fires as per kg fuel consumed.

§ Not quantified.

¶ Name used by Pouwels *et al.*

be due to the fact that our fires were smoldering only without the flaming phase, while their fires included the flaming phase. The different species of pine burned, and different sampling and extraction methods will also have an effect. We did not detect any anisaldehyde, whereas they reported 0.7 mg kg<sup>-1</sup>. Either anisaldehyde was present below our detection limits, or it was not emitted in the smoldering of ponderosa pine. In addition, they reported 1-methyl-3,4-dimethoxybenzene, whereas we report 4-ethylguaiacol at the same retention sequence. Both compounds have a molecular ion of 152. 4-ethylguaiacol is a more likely pyrolysis product from lignin than 1-methyl-3,4-dimethoxybenzene and has been reported previously (Pouwels *et al.*, 1987; Faix *et al.*, 1990).

#### Noncondensable components

The noncondensable gases consisted of CO<sub>2</sub>, CO, methane, ethene and ethane with yields shown in Table 4. The molar ratio of emitted CO<sub>2</sub> to CO<sub>2</sub> + CO

Table 4. Yields of components in smoke noncondensates

Compound	Yield (g kg <sup>-1</sup> )*	RSD (%)
Carbon dioxide	870	15
Carbon monoxide	150	28
Methane	3	18
Ethene	2.2	10
Ethane	0.4	25

\* The mean yield from three separate fires as g kg<sup>-1</sup> fuel consumed.

is described as combustion efficiency (Hao and Ward, 1993), which ranged from 71 to 83% for the three fires, with a mean value of 79% (RSD = 6%). This value is typical of smoldering combustion of biomass (Hao and Ward, 1993) and is lower than would be expected for flaming combustion of the same fuel. The major

Table 5. Preliminary estimates of exposure levels

Compound	Molar ratio to CO	Exposure level* (ppm)
Acetol	$3.0 \times 10^{-3}$	0.12
Vinyl acetate	$6.5 \times 10^{-3}$	0.26
Pyruvic aldehyde	$5.2 \times 10^{-3}$	0.21
Acetic acid	$1.4 \times 10^{-2}$	0.55
Formic acid	$3.9 \times 10^{-3}$	0.16
Methanol	$2.5 \times 10^{-2}$	1.00

\* Based on a 40 ppm CO exposure level.

hydrocarbon was methane. Of the  $C_2$  hydrocarbons, ethene exceeded ethane, with only a trace of ethyne present [cf. Lobert *et al.* (1991)]. Higher hydrocarbons were present in much smaller amounts than the  $C_2$  series, but were not determined.

#### Ratios of the yields of condensable compounds to the yield of CO

The concentrations of condensable compounds would be difficult to measure in the plumes of actual wildland fires to which firefighters are exposed. However, it is possible to measure CO exposure levels with personal monitors. Exposure levels of the condensable compounds during smoldering combustion may then be estimated on the basis of (1) the molar ratios between the yields of these compounds to the yield of CO measured in laboratory fires, and (2) the CO concentrations measured in the field during the smoldering phase of wildland fires. The molar ratios of the major condensable emissions to CO, along with preliminary estimates of exposure levels of these compounds, based on a CO exposure level of 40 ppm, are presented in Table 5. Ward *et al.* (1993) used a similar technique to estimate the release of benzene from all prescribed fires used in the U.S.A. by calculating the ratio of benzene emitted to CO emitted. We are currently investigating whether these ratios can be extended to include other fuel components (e.g. bark, needles, litter, duff, humus) and types of fires.

#### CONCLUSIONS

Several conclusions may be drawn from our experiments as follows:

- (1) These are the first measurements of the yields of the condensable compounds emitted from simulated smoldering combustion conditions for wildland fires.
- (2) The experiments and measurements are reasonably reproducible to the extent indicated, given the large number of uncontrolled variables associated with the fires
- (3) Most of the condensable products are produced from pyrolysis of lignin and polysaccharides.
- (4) Preliminary estimates for firefighter exposures to

some of the condensable compounds in smoldering smoke from wild and prescribed fires can be made.

- (5) The number of experiments needs to be expanded to other fuel types, fire conditions, and larger scale fires for verification of the results.

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#### REFERENCES

- Crutzen P. J. and Andreae M. O. (1990) Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles. *Science* **250**, 1669–1678.
- DeGroot W. F., Pan W.-P., Rahman M. D. and Richards G. N. (1988) First chemical events in pyrolysis of wood. *J. analyt. appl. Pyrol.* **13**, 221–231.
- Edye L. A. and Richards G. N. (1991) Analysis of condensates from wood smoke: Components derived from polysaccharides and lignins. *Envir. Sci. Technol.* **25**, 1133–1137.
- Faix O., Meier D. and Fortmann I. (1990) Thermal degradation products of wood: gas chromatographic separation and mass spectrometric characterization of monomeric lignin derived products. *Holz als Roh-und Werkstoff* **48**, 281–285.
- Faix O., Fortmann I., Bremer J. and Meier D. (1991) Thermal degradation products: A collection of electron-impact (EI) mass spectra of polysaccharide derived products. *Holz als Roh-und Werkstoff* **49**, 299–304.
- Hao W. M. and Ward D. E. (1993) Methane production from global biomass burning. *J. geophys. Res.* **98**, 20,657–20,661.
- Hao W. M. and Liu M.-H. (1994) Spatial and temporal distribution of tropical biomass burning with  $5^\circ \times 5^\circ$  resolution. *Global biogeochem. Cycles* (in press).
- Hawthorne S. B., Krieger M. S., Miller D. J. and Mathiason M. B. (1989) Collection and quantitation of methoxylated phenol tracers for atmospheric pollution from residential wood stoves. *Envir. Sci. Technol.* **23**, 470–475.
- Hawthorne S. B., Miller D. J., Langenfeld J. J. and Krieger M. S. (1992) PM-10 high-volume collection and quantitation of semi- and nonvolatile phenols, methoxylated phenols, alkanes, and polycyclic aromatic hydrocarbons from winter urban air and their relationship to wood smoke emissions. *Envir. Sci. Technol.* **26**, 2251–2262.
- Kakimoto M. (1992) Simultaneous determination of sorbic acid, dehydroacetic acid and benzoic acid by gas chromatography-mass spectrometry. *J. Chromatog.* **594**, 253–257.
- Lobert J. M., Scharffe D. H., Hao W. M., Kuhlbusch T. A., Seuwen R., Warneck P. and Crutzen P. J. (1991) Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds. In *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications* (edited by Levine J. S.), pp. 289–304. MIT Press, Cambridge, MA.
- Pouwels D. A., Tom A., Eijkel G. B. and Bonn J. J. (1987) Characterisation of beech wood and its holocellulose and xylan fractions by pyrolysis-gas chromatography-mass spectrometry. *J. analyt. appl. Pyrol.* **11**, 417–436.
- Simoneit B. R. T., Rogge W. F., Mazurek M. A., Standley L. J., Hildemann L. M. and Cass G. R. (1993) Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Envir. Sci. Technol.* **27**, 2533–2541.
- Ward D. E., Susott R. A., Kauffman J. B., Babbitt R. E., Cummings D. L., Dias B., Holben B. N., Kaufman Y. J.,

- Rasmussen R. A. and Setzer A. W. (1992) Smoke and fire characteristics for cerrado and deforestation burns in Brazil: Base-B experiment. *J. geophys. Res.* **97**, 14, 601–14, 619.
- Ward D. E., Peterson J. and Hao W. M. (1993) An inventory of particulate matter and air toxic emissions from prescribed fires in the USA for 1989. In *Proceedings of the 86th Annual Meeting and Exhibition of the Air and Waste Management Association*, Denver, Colorado.